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(21) International Application Number: PCT/GB94/01181 (22) International Filing Date: 1 June 1994 (01.06.94) (30) Priority Data: 93114023 2 June 1993 (02.06.93) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): LIGGAT, John, Jamieson [GB/GB]; 64 Briggs Avenue, Middlesbrough, Cleveland TS6 6XN (GB). O'BRIEN, Gregory [US/US]; 7 Beechwood Circle, Hockessin, DE 19707 (US). (74) Agents: MANNION, Sally, Kim et al.; Group Patents Services Dept., P.O. Box 6, Shire Park, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD (GB).	(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BI, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: PROCESSING OF POLYESTERS (57) Abstract Method of retarding age embrittlement of polyester comprising heat treating the polyester after preparation by cooling below 90 °C and then heating at 90 °C to 160 °C within 24 hours of preparation, and a polyester composition in which ageing is substantially retarded compared to the non-heat treated polyester. The invention encompasses the polyester composition which has been subjected to the method.		

PROCESSING OF POLYESTERS

THIS INVENTION relates to processing of polyesters and in particular to producing shaped articles less liable to embrittlement.

It has been disclosed by de Koning et al in Polymer 92, 33, (15), 3295-3297 that whereas one such polyester poly(R)-3-hydroxybutyrate when freshly moulded shows ductile behaviour, within several weeks at room temperature the tensile modulus doubles and elongation at break drops below 10%. A typical feature of such ageing is that it can be partly reversed by heat or mechanical strain. Using mild 'deageing' treatment, the improvement in ductility is only small and temporary, but heating at above 100°C restores the original mechanical properties and prevents or at least retards ageing to a large extent.

It has now been found that such age-embrittlement can be prevented or slowed by applying the heat treatment to shaped articles made substantially of polyhydroxybutyrate (PHB), polyhydroxybutyrate-co-valerate (PHBV) and/or other polyhydroxyalkanoates before they have undergone significant ageing.

Thus according to the invention there is provided a polyester composition comprising polyhydroxyalkanoate (PHA) in which ageing of the polyester is retarded characterised in that after preparation the polyester is cooled to below 90°C and then heat treated at 90°C to 160°C within 24 hours of preparation, and in that subsequent ageing is substantially retarded compared to the non-heat treated polyester.

In a further aspect of the invention there is provided a shaped article at least partly made of polyhydroxyalkanoate (PHA) in which ageing of the polyester is substantially retarded characterised in that after preparation the article is allowed to cool to below 90°C is heat treated at 90°C to 160°C within 24 hours of preparation, and in that subsequent ageing is substantially retarded compared to the non-heat treated polyester.

"Ageing" means deterioration of the mechanical properties of polymer with time, for example, ductility and tensile strength. Loss of mechanical properties can be measured by measurements indicative of ageing, for example, elongation to break and impact resistance (Izod).

In the present context "substantially retarded" means that for

Typically $C_m H_n$ contains 2-5 carbon atoms in the polymer chain and the remainder (if any) in a side chain. In very suitable polyesters m is 3 or 4, n is $2m$ and especially there are units with $m = 3$ and $m = 4$ copolymerised together and with respectively a C_1 and C_2 side chain on the carbon next to oxygen in the chain. Particular polyesters contain a preponderance of $m = 3$ units, especially homopolymer (PHB) or with at least 70 mol %, preferably 70-98% of such units, the balance (if any) being units in which $m = 4$ (PHBV). The molecular weight of the PHA is preferably over 50000, especially over 100000, up to eg 2×10^6 .

The PHA is conveniently a blend of two or more polymers or copolymers differing in the value of m . A particular example contains

- (a) PHA consisting essentially of Formula I units in which 2-5 mol % of units have $m = 4$, the rest $m = 3$; and
- (b) PHA consisting essentially of Formula I units in which 5-30 mol% of units have $m = 4$, the rest $m = 3$.

In each such PHA there are side chains as above mentioned. The proportions in such a blend are preferably such as give an average $m = 4$ content in the range 4 - 20 mol %.

In each such PHA having units with $m = 3$ and/or $m = 4$ there may be very small, typically fractional, percentages of units having higher values of m .

Typically the composition contains microbiologically produced PHA to the extent of over 50% w/w, especially over 80% w/w.

PHA comprising hydroxybutyrate units and hydroxyvalerate units includes PHBV copolymers containing up to 1 mol percent of other oxyalkanoate units whether introduced deliberately or not.

The polyhydroxyalkanoate is preferably polyhydroxy-butyrate (PHB) or polyhydroxybutyrate-co-valerate (PHBV), which may be 3-hydroxy or 4-hydroxy or a mixture of both. Especially preferred are the (R)-3-hydroxy forms of PHB and PHBV.

The PHA is preferably a fermentation product, especially of a microbiological process in which a microorganism lays down PHA during normal growth or is caused to do so by cultivation in the absence of one or more nutrients necessary for cell multiplication. The microorganism may be wild or mutated or may have had the necessary genetic material

or fibres, including multilayer coatings, films or fibres.

The plasticiser is any material capable of plasticising polyester, i.e. capable of improving the ductility of the polyester and especially any material capable of plasticising PHB or PHBV. There may be one or more plasticisers present. For the ratio of plasticiser to PHA the range up to and including 40 phr w/w, preferably 1 to 40 phr w/w includes most of the likely uses and for making effectively rigid but not brittle articles the range 5-20 especially 6-12, phr w/w is generally suitable.

Examples of suitable plasticisers are

- (a) high-boiling esters of polybasic acids, such as phthalates, isophthalates, citrates, fumarates, glutamate, phosphates or phosphites. The esterified radicals may be for example $C_1 - C_{12}$ alkyl, aryl, aralkyl or aralkyl. Particular examples are dioctyl-, dibutyl- and dodecyl- phthalates and dialkylalkylene oxide glutamate (Plasthall 7050);
- (b) high boiling esters and part- of polyhydric alcohols, especially glycols, polyglycols and glycerol. The acid-derived radical of the ester typically contains 2-10 carbon atoms. Examples are triacetin, diacetin and glyceryl dibenzoate;
- (c) aromatic sulphonamides such as paratoluene sulphonamide.

A particularly preferred plasticiser is a doubly esterified hydroxycarboxylic acid having at least 3 ester groups in its molecule.

"Doubly esterified" means that at least some of the hydroxy groups of the hydroxycarboxylic acid are esterified with a carboxylic acid and at least some of the carboxy groups thereof are esterified with an alcohol or phenol. Preferably at least the hydroxycarboxylic acid from which the ester is derived is aliphatic or cycloaliphatic. Its backbone structure (that is, apart from carboxy groups) preferably contains 2-6 carbon atoms. It contains preferably 2-4 carboxy groups and 1-3 hydroxy groups; and preferably the number of carboxy groups exceeds the number of hydroxy groups.

The groups with which the carboxy groups are esterified contain preferably 1-7, especially 2-5 carbon atoms. In the ester molecule they can be the same or different. Preferably they are aliphatic. For thermal stability but biodegradability such aliphatic groups preferably have

vacuo, or in water or a fluid which does not interfere with the integrity of the polyester, or in a mould. Heat transfer can be by conduction, radiation, convection or resistive heating. Heat transfer methods may include ovens, water baths and hot rollers. A preferred form of heat transfer is by infra red radiation, for example, black body and quartz tubes. The shaped article is generally subjected to infra red radiation for 30 seconds to 15 minutes, preferably 30 seconds to 10 minutes.

The shaped articles may be run through the oven or other heating method on a continuous belt at a speed which is optimal to enable the shaped article to reach the correct temperature. A preferred method is to have a multi-zone system, preferably a 2 zone heat system in which the first zone gives a rapid rate of heating (i.e. the actual temperature in the zone may higher than that to be achieved by the shaped article) to bring it to the actual temperature required and then in the second zone the shaped article is maintained at the actual temperature to be achieved for the desired time period.

The invention provides methods of making the composition by mixing its components. If desired, this may be effected in a solvent, such as a halogenated hydrocarbon or alkylene carbonate. Such a method is convenient for coating or for centrifugal spinning of fibres. More conveniently, if a plasticiser is present, the plasticiser is mixed with powdered dry polymer and the mixture is treated in conditions of shear, such as in a plastic mill or extruder. The product is then granulated and used as feed for a shaping operation such as extrusion, injection moulding, injection blow-moulding or compression moulding.

The composition is especially useful for making the following shaped articles: films, especially for packaging, fibres, non-woven fabrics, extruded nets, personal hygiene products, bottles and drinking vessels, agricultural and horticultural films and vessels, ostomy bags, coated products (such as paper, paperboard, non-woven fabrics), agricultural and horticultural films and vessels, slow-release devices. Alternatively, the polymer composition with suitable additives can be used as an adhesive.

The invention is now further described, but is not limited by, the following examples.

Formulation and test procedures

heat treated at 110°C for 1 hour. The bars were tested for elongation to break over various periods. The lower the elongation to break the less ductile the polymer. Results are shown in Table 1 as percentage elongation to break.

Table 1

	Ageing time after heat treatment(days)				
	0	1	3	7	28
Control	459.3	15.3	-	13.8	12.8
treated	282.5	-	44.8	30.6	29.0

(-) means not tested.

It is evident that for the heat treated polymer the extension to break, although initially considerably less than for the non-heat treated polymer, decreases less rapidly over a period of time to a level significantly (over 100%) and usefully higher than that of the untreated polymer.

Example 2

The experiment of Example 1 was repeated using plasticised homopolymer (1 phr BN as nucleant and 20 phr Diolpate PPA 350 as plasticiser).

The bars were released directly after moulding. Within 30 seconds of demoulding the bars were heat treated at 110°C for 1 minute. The bars were tested for extension to break and the values are represented as percentage extension to break.

Table 2

	Ageing time after treatment (days)					
	0	1	7	28	84	185
Control	619	340	21.2	17.4	14.9	11.95
treated	540	427	103	34.9	25.8	21.9

It is evident that the extension to break for the heat treated polymer, although starting from a lower value, does not decrease as rapidly as the

CLAIMS

1. Polyester composition comprising polyhydroxyalkanoate (PHA) in which ageing of the polyester is retarded characterised in that after preparation the polyester is cooled to below 90°C and then heat treated at 90°C to 160°C within 24 hours of preparation, and in that subsequent ageing is substantially retarded compared to a non-heat treated polyester.
2. Polyester composition according to claim 1 wherein the composition contains a plasticiser.
3. Polyester composition according to claim 2 wherein the composition contains up to and including 40 phr w/w of plasticiser.
4. Polyester composition according to claim 1 which consists essentially of polyhydroxyalkanoate (PHA).
5. Polyester composition according to any of the previous claims wherein the composition is heat treated at 100°C to 140°C.
6. Polyester composition according to any of the previous claims wherein the composition shows at least 40% improvement in brittleness or ductility compared to the non-heat treated polyester composition.
7. Polyester composition according to any of the previous claims wherein the polyhydroxyalkanoate is either polyhydroxybutyrate or polyhydroxybutyrate-co-valerate.
8. Polyester composition according to Claim 7 wherein the polyhydroxybutyrate is poly-(R)-3-hydroxybutyrate and the polyhydroxybutyrate-co-valerate is poly-(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate.
9. Shaped article at least partly made of polyhydroxyalkanoate (PHA) in which ageing of the polyester is retarded characterised in that after preparation the article is allowed to cool to below 90°C is heat treated at 90°C to 160°C within 24 hours of preparation, and in that subsequent ageing of the polyester is substantially retarded compared to a non-heat treated polyester.
10. Method of retarding age embrittlement of polyester comprising heat treating said polyester characterised in that after preparation

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 94/01181

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08G63/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08G C08J C12P C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POLYMER vol. 33, no. 15, 1992, OXFORD pages 3295 - 3297 G. J. M. DE KONING ET AL 'Ageing phenomena in bacterial poly[(R)-3-hydroxybutyrate]' cited in the application	1,4-18
Y	see page 3295, introduction ---	2,3
Y	WO,A,92 01548 (E.I. DU PONT DE NEMOURS AND CO) 6 February 1992 see claims 1-9 --- -/--	2,3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *Z* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. App. No.

PCT/GB 94/01181

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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